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Supplementary Material

Limitations of GC-QTOF-MS Technique in Identification of Odorous Compounds from Wastewater: The Application of GC-IMS as Supplement for Odor Profiling

Wei Gao [1,2], Xiaofang Yang [1,*], Xinmeng Zhu [1,2], Ruyuan Jiao [1], Shan Zhao [3], Jianwei Yu [1] and Dongsheng Wang [1,2,4,*]

[1] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; weigao_st@rcees.ac.cn (W.G.); xmzhu_st@rcees.ac.cn (X.Z.); ryjiao@rcees.ac.cn (R.J.); jwyu@rcees.ac.cn (J.Y.)
[2] University of Chinese Academy of Sciences, Beijing 100049, China
[3] Research and Development Center, Beijing Drainage Group Co., Ltd., Beijing 100124, China; zhaoshan@bdc.cn
[4] School of Environmental Studies, China University of Geosciences, Wuhan 430074, China
* Correspondence: xfyang@rcees.ac.cn (X.Y.), wgds@rcees.ac.cn (D.W.)

The supplementary material contains one text for description of background information of wastewater treatment plants, three Figures and six Tables.

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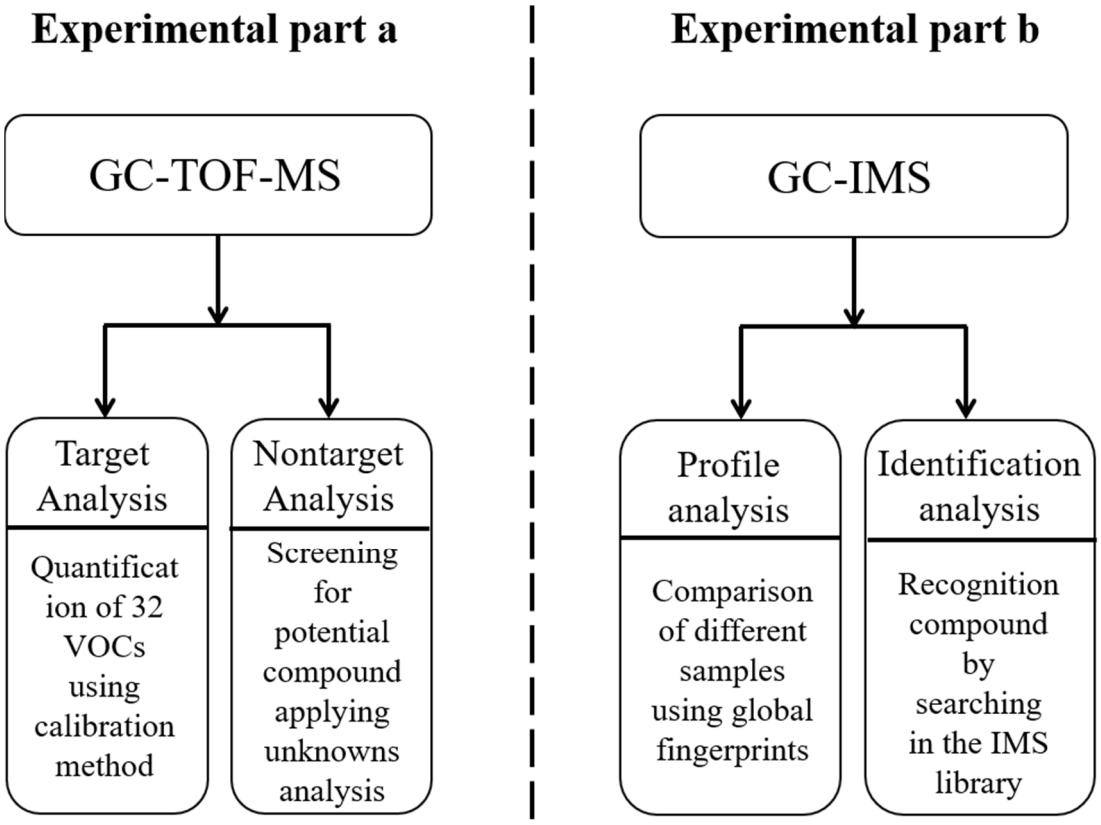

Figure S1. The experimental design of analytical method applied for wastewater samples.

- The background information of wastewater treatment plants.

The treatment capacity of wastewater treatment plants is 600000 m^3 / D, the coefficient of variation is 1.3 and the peak flow is 780000 m^3 / D. The planned drainage area is about 223.5km^2, serving 2.415 million citizens. The plant has 8 primary sedimentation tanks, 4 aeration tanks and 16 secondary sedimentation tanks. The aeration tank was composed of anaerobic tank and aerobic tank, which can provide appropriate oxygen for microorganisms. This wastewater treatment plant adopts anaerobic, aerobic and phosphorus removal processes (A^2/O) which is shown in Figure S2.

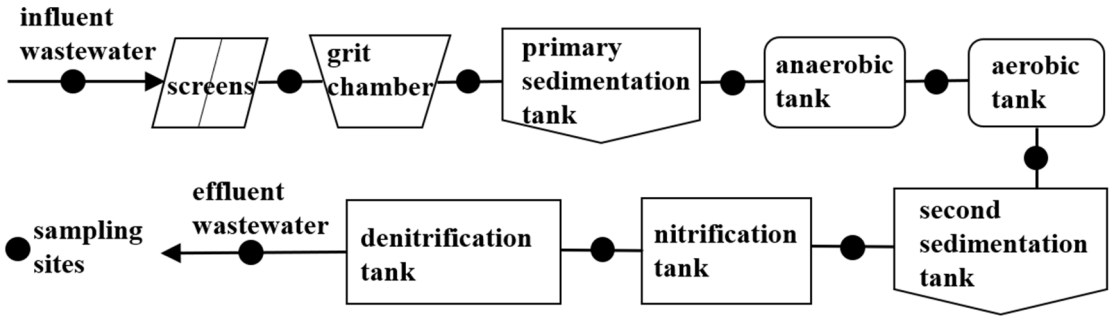

Figure S2. Sample sites at municipal wastewater treatment plants.

Table S1. The information of standard compounds used for GC-IMS (gas chromatography-ion mobility spectrometry) calibration.

Count	Compound	CAS	Formula	MW	RI	Rt/s	Dt/RIPrel
1	2-nonanone	821-55-6	C9H18O	142.2	1095.6	697.14	1.7565
2	2-Octanone	111-13-7	C8H16O	128.2	996.5	468.35	1.6288

3	2-heptanone	110-43-0	C7H14O	114.2	892.2	318.88	1.5012
4	2-Hexanone	591-78-6	C6H12O	100.2	784.2	225.58	1.3709
5	2-Pentanone	107-87-9	C5H10O	86.1	688.6	173.23	1.2446
6	2-Butanone	78-93-3	C4H8O	72.1	589.4	134.16	1.1159

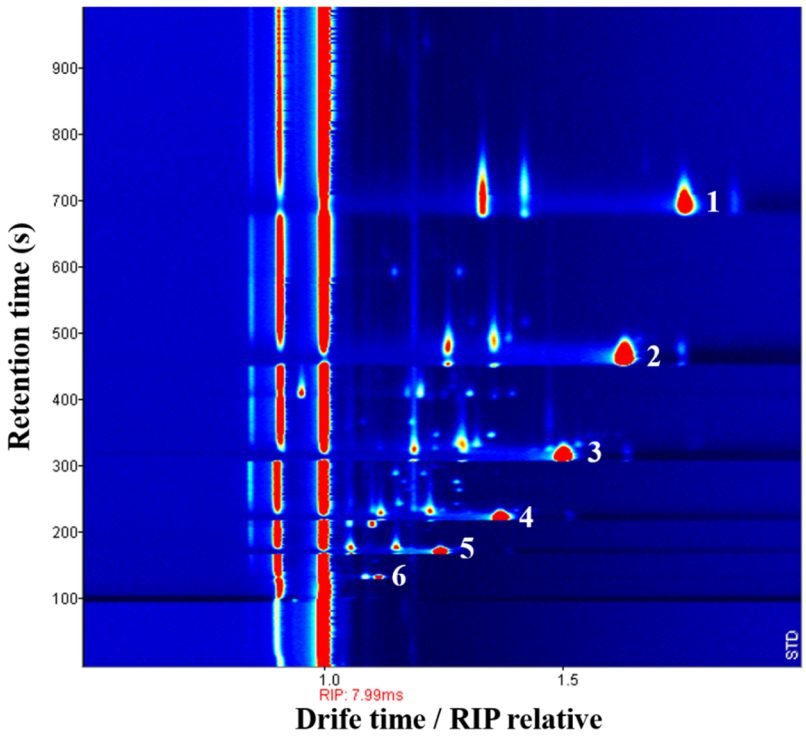

Figure S3. The GC-IMS (gas chromatography-ion mobility spectrometry) chromatogram of mixing standards.

Table S2. Information of identified compounds in GC-QTOF-MS (gas chromatography quadrupole-time-of-flight mass spectrometry).

Compound	CAS	Formula	RT	MF
Ammonium sulfamate	7773-06-0	H6N2O3S	3.2649	72.8
Dimethyl sulfone	67-71-0	C2H6O2S	4.1383	76.4
Disulfide, dimethyl	624-92-0	C2H6S2	4.1760	73.6
Toluene	108-88-3	C7H8	4.7061	86.7
Trimethylene oxide	503-30-0	C3H6O	6.0351	83.1
Chlorobenzene	108-90-7	C6H5Cl	7.5094	75.3
4-Methylthiazole	693-95-8	C4H5NS	7.5381	81.7
Cyanamide, dimethyl-	1467-79-4	C3H6N2	8.3079	74.7
2-Propenal	107-02-8	C3H4O	8.6501	88.8
2-Propynoic acid, methyl ester	922-67-8	C4H4O2	10.4499	75.2
Propanoic acid, anhydride	123-62-6	C6H10O3	12.1359	73.9
Dimethyl trisulfide	3658-80-8	C2H6S3	12.9376	79.2
2-Methylthiolane, S, S-dioxide	1003-46-9	C5H10O2S	13.1160	80.7
4-Cyanoimidazole	57090-88-7	C4H3N3	13.6919	87.1
Phenol, 2-chloro-	95-57-8	C6H5ClO	14.2064	71.5
Phenol	108-95-2	C6H6O	14.4232	83.9
2-Undecen-4-ol	22381-86-8	C11H22O	14.5495	71.0
Pyridine, 4-methoxy-	620-08-6	C6H7NO	14.8330	90.6
4-Pyridinamine, N, N-dimethyl-	1122-58-3	C7H10N2	14.8876	74.6
1,4-dichlorobenzene	106-46-7	C6H4Cl2	15.0615	87.2

P-cymene	99-87-6	C10H14	15.7431	87.2
Ethanone,2,2-dihydroxy-1-phenyl-	1075-06-5	C8H8O3	17.8701	91.7
Pyrazine, 2,6-diethyl-	13067-27-1	C8H12N2	18.5712	85.7
Benzyl alcohol	100-51-6	C7H8O	18.9109	93.5
Indan, 1-methyl-	767-58-8	C10H12	18.9781	72.5
Benzene, 4-ethyl-1,2-dimethyl-	934-80-5	C10H14	20.1689	93.0
(E)-1-Phenyl-1-butene	1005-64-7	C10H12	21.2089	90.3
Pyrazine, 2,3-diethyl-5-methyl-	18138-04-0	C9H14N2	22.2976	78.0
Naphthalene	91-20-3	C10H8	23.2493	96.7
2-Furancarboxylic acid, hydrazide	3326-71-4	C5H6N2O2	23.4877	73.5
1-methyl-1-indanol	64666-42-8	C10H12O	23.5908	76.0
3-Carene	13466-78-9	C10H16	23.8500	83.4
Tetrasulfide, dimethyl	5756-24-1	C2H6S4	24.8379	81.8
Furan, 3-phenyl-	13679-41-9	C10H8O	25.2654	72.2
1H-Indene,2,3-dihydro-1,1-dimethyl-	4912-92-9	C11H14	26.3704	92.4
Heptane,4-ethyl-2,2,6,6-tetramethyl-	62108-31-0	C13H28	27.0193	71.8
2-tert-Butyltoluene	1074-92-6	C11H16	27.7501	84.1
Indole	120-72-9	C8H7N	28.7808	88.4
Naphthalene, 2-methyl-	91-57-6	C11H10	29.0119	88.5

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Table S3. Target compounds, CAS Number, Boiling point, retention index (RI), retention time (RT), quantitative ion (Ti) and qualitative ion (Qi) used for detection of targeted compounds.

Compound	CAS	Boiling point	RI	RT/min	Ti	Qi
Dibromomethane	74-95-3	96.0	700	3.255	173.8492	92.9330
1,3-dichloropropylene	10061-02-6 /10061-01-5	104.0	750	4.024	74.9991	77.0012
Toluene	108-88-3	110.6	763	4.788	91.0540	92.0613
Dibromochloromethane	124-48-1	119.0	800	5.476	128.8919	126.8942
Tetrachloroethylene	127-18-4	121.2	814	5.910	165.8712	128.9049
1,2-dibromoethane	106-93-4	131.0	806	5.860	106.9488	108.9468
Chlorobenzene	108-90-7	132.2	849	7.509	112.0072	77.0384
Ethylbenzene	100-41-4	136.2	855	8.007	91.0540	106.0772
1,1,1,2-tetrachloroethane	630-20-6	138.0	869	7.487	130.9212	132.9183
Xylene	106-42-3 /108-38-3 /95-47-6	138.5	865/866/887	8.350	91.0542	106.0774
Styrene	100-42-5	146.0	893	9.340	104.0616	78.0460
1,1,2,2-tetrachloroethane	79-34-5	146.4	916	10.391	82.9447	84.9417
Bromoform	75-25-2	149.5	892	8.969	172.8418	174.8398
Isopropylbenzene	98-82-8	152.4	921	10.829	105.0696	120.0930
Bromobenzene	108-86-1	156.2	960	10.982	77.0384	155.9567
1,2,3-trichloropropane	96-18-4	156.8	938	10.765	74.9910	109.9679
2-chlorotoluene	95-49-8	158.0	955	12.047	91.0599	126.0228
N-propylbenzene	103-65-1	159.2	953	12.228	120.0917	78.0440
4-chlorotoluene	106-43-4	162.0	959	12.301	91.0539	126.0227
Trimethylbenzene	108-67-8 /95-63-6	164.7	972/990	12.946	105.0698	120.0930
Tert-butylbenzene	98-06-6	169.0	975	14.131	119.0854	91.0541
1,3-dichlorobenzene	541-73-1	172.0	1018	14.642	145.9683	147.9653
Sec-butylbenzene	135-98-8	173.0	994	14.993	105.0695	134.1083
1,4-dichlorobenzene	106-46-7	174.0	1021	15.023	145.9683	147.9654
P-cymene	99-87-6	177.1	1025	15.717	119.0853	91.0539
1,2-dichlorobenzene	95-50-1	180.4	1043	16.071	145.9683	147.9654
N-butylbenzene	104-51-8	182.1	1054	17.273	91.0542	92.0615
1,2-dibromo-3-chloropropane	96-12-8	195.0	1092	18.499	156.9234	74.9995
Hexachlorobutadiene	87-68-3	213.0	1231	24.937	224.8404	226.8375
Naphthalene	91-20-3	217.9	1182	23.234	128.0617	102.0462
1,2,3-trichlorobenzene	87-61-6	218.0	1206	24.613	181.9263	179.9291
1,2,4-trichlorobenzene	120-82-1	221.0	1193	22.957	179.9292	181.9262

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Table S4. Precision (intra-day) expressed as RSD (%), and accuracy expressed as recovery (%), for the target VOCs (volatile organic compounds). The correlation coefficient, Linear range, LOD (ng/L) and LOQ (ng/L) of the method for determining the concentration of VOCs.

Compound	RSD (%, n=5)		Recovery (%) ±SD		R^2	Linear range	LOD	LOQ
	50 ng/L	500 ng/L	50 ng/L	500 ng/L				
Dibromomethane	6.25	10.18	115.05±11.32	100.49±5.33	0.9915	25-1000	7.1	23.8
1,3-dichloropropylene	8.74	0.84	84.78±5.57	101.10±1.08	0.9953	200-1000	50.0	166.6
Toluene	4.58	1.70	99.02±9.28	96.12±3.53	0.9902	50-1000	8.3	27.7
Dibromochloromethane	5.15	5.88	71.97±11.28	95.88±3.48	0.9941	10-1000	2.3	7.6
Tetrachloroethylene	1.17	10.00	98.62±8.31	104.60±10.24	0.9952	5-1000	0.5	1.8
1,2-dibromoethane	5.26	4.05	72.74±9.76	107.87±3.69	0.9936	10-1000	3.0	10.0
Chlorobenzene	2.66	5.08	96.08±5.16	85.86±4.90	0.9994	5-1000	1.2	3.9
Ethylbenzene	1.27	0.81	113.71±5.73	91.29±10.49	0.9996	50-1000	8.9	30.0
1,1,1,2-tetrachloroethane	6.17	11.11	82.91±4.33	108.56±2.58	0.9925	10-1000	2.5	8.3
Xylene	3.69	2.04	100.61±9.41	93.39±8.41	0.9998	150-1000	36.0	120.0
Styrene	2.08	8.31	72.57±7.78	70.11±2.71	0.9997	50-2000	12.5	41.6
1,1,2,2-tetrachloroethane	5.69	1.00	74.29±7.83	98.50±2.51	0.9976	10-1000	2.1	6.9
Bromoform	7.40	7.45	71.87±16.27	111.88±3.57	0.9945	50-1000	12.5	41.6
Isopropylbenzene	9.25	3.36	77.49±16.46	91.44±13.81	0.9972	15-1000	3.2	10.7
Bromobenzene	3.08	4.77	108.00±8.36	78.91±3.28	0.9982	50-1000	12.0	40.0
1,2,3-trichloropropane	5.74	1.65	118.14±7.64	102.40±1.48	0.9985	25-1000	7.1	23.6
2-chlorotoluene	4.46	1.10	71.99±2.36	101.67±1.38	0.9998	50-1000	12.5	41.6
N-propylbenzene	6.79	9.35	110.31±12.92	77.66±15.81	0.9979	50-1000	15.0	50.0
4-chlorotoluene	2.10	7.63	101.10±2.02	100.29±4.96	0.9996	50-1000	8.3	27.7
Trimethylbenzene	8.69	6.29	90.70±9.95	100.10±9.24	0.9986	20-1000	6.0	20.0
Tert-butylbenzene	8.16	7.55	99.54±4.16	103.89±5.67	0.9982	10-1000	1.7	5.7
1,3-dichlorobenzene	4.33	3.66	116.05±3.88	94.10±4.04	0.9996	10-2000	2.8	9.3
Sec-butylbenzene	7.82	6.58	94.45±3.91	104.08±4.30	0.9955	10-1000	2.2	7.2
1,4-dichlorobenzene	8.78	8.10	99.29±5.90	101.45±5.30	0.9985	50-2000	8.9	29.8
P-cymene	3.43	8.37	93.86±8.95	104.90±8.85	0.9986	10-1000	2.1	7.1
1,2-dichlorobenzene	7.07	2.37	74.53±2.21	98.50±2.49	0.9991	50-2000	7.9	26.3
N-butylbenzene	4.64	6.52	82.48±7.71	86.36±17.71	0.9961	25-1000	4.3	14.4
1,2-dibromo-3-chloropropane	5.42	10.28	101.84±4.56	102.74±4.39	0.9997	5-2000	0.5	1.7
Hexachlorobutadiene	7.45	4.53	91.56±6.44	104.90±13.42	0.9946	1-1000	0.2	0.7
Naphthalene	5.67	7.95	96.33±4.26	102.29±10.26	0.9996	10-2000	2.2	7.3
1,2,3-trichlorobenzene	3.31	4.85	109.58±5.11	94.99±4.51	0.9987	25-2000	3.3	11.0
1,2,4-trichlorobenzene	5.30	3.44	77.47±5.00	87.40±4.17	0.9997	5-2000	0.8	2.7

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Table S5. The quantitative results of wastewater samples (ng/L).

Process	Tetrachloroethylene	Chlorobenzene	Ethylbenzene	1,4-dichlorobenzene	P-cymene	Naphthalene
IW	79.05	10.22	28.23	176.11	189.22	276.69
GBI	97.71	36.14	46.18	395.42	346.69	458.54
GBO	142.57	37.17	43.11	354.26	325.00	452.93
PSO	158.71	28.59	39.74	213.07	258.20	284.21
ANO	199.63	6.42	-*	286.25	-	64.65
AO	208.46	16.79	-	337.14	-	49.27
SSO	46.83	1.39	-	109.35	-	32.16
NO	9.37	40.18	-	96.22	-	33.13
DNO	10.78	41.22	-	101.36	-	37.36

*-, not detected.

Note: IW: influent wastewater, GBI: rotational flow grit basin inlet, GBO: rotational flow grit basin outlet, PSO: primary sedimentation tank outlet, ANO: anaerobic tank outlet, AO: aerobic tank outlet, SSO: secondary sedimentation tank outlet, NO: nitrification outlet, DNO: denitrification outlet.

Table S6. Information of identified compounds in GC-IMS.

Compound	CAS	Formula	RI	Rt/s	Dt/RIPrel
Acetone	67-64-1	C3H6O	496.1	135.11	1.1156
Tert-butylmethylether	1634-04-4	C5H12O	563.7	162.22	1.1194
2-butanone	78-93-3	C4H8O	587.4	172.93	1.2433
Acetic acid	64-19-7	C2H4O2	587.5	172.99	1.0553
2-methyl-1-propanol	78-83-1	C4H10O	620.7	189.24	1.1683
3-methylbutanal	590-86-3	C5H10O	644.5	201.81	1.3998
2,3-pentanedione	600-14-6	C5H8O2	683.1	224.05	1.2200
Ethyl propanoate	105-37-3	C5H10O2	686.7	226.24	1.1515
1-propene-3-methylthio	10152-76-8	C4H8S	690.0	228.57	1.0400
Propanoic acid	79-09-4	C3H6O2	696.2	233.67	1.1040
Pentanal	110-62-3	C5H10O	698.0	235.21	1.1879
3-hydroxy-2-butanone	513-86-0	C4H8O2	704.2	240.56	1.0583
3-methyl-1-butanol	123-51-3	C5H12O	720.5	255.11	1.2419
2-hexanol	626-93-7	C6H14O	788.0	325.44	1.2717
Isovaleric acid	503-74-2	C5H10O2	827.1	374.31	1.4797
Heptanal	111-71-7	C7H14O	897.2	481.73	1.3371
Methional	3268-49-3	C4H8OS	928.0	541.36	1.3898